

SOLITONS IN NEARLY COMMENSURATE ORGANIC CHARGE TRANSFER CRYSTALS

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Résumé - Des études de diffusion diffuse des rayons X, du magnétisme et de la conductivité électrique du (N-méthylphénazinium)_x (phénazine)_{1-x} (tétracyanoquinodiméthane) [(NMP)_x(Phén)_{1-x}(TCNQ)] montrent la formation de défauts pour $0,50 \lesssim x \lesssim 0,54$. Ceux-ci peuvent s'interpréter comme provenant de la formation de solitons dans un système électronique quasi-unidimensionnel fortement corrélé ayant un taux de remplissage proche de la limite de un quart.

Abstract - X-ray diffuse scattering, magnetic, and conductivity studies of (N-methylphenazinium)_x (phenazine)_{1-x} (tetracyanoquinodimethane) [(NMP)_x(Phen)_{1-x}(TCNQ)] show the formation of defect states for $0.50 \lesssim x \lesssim 0.54$. These results are in agreement with the formation of solitons in a highly correlated quasi-one-dimensional system near the quarter-filled-band limit.

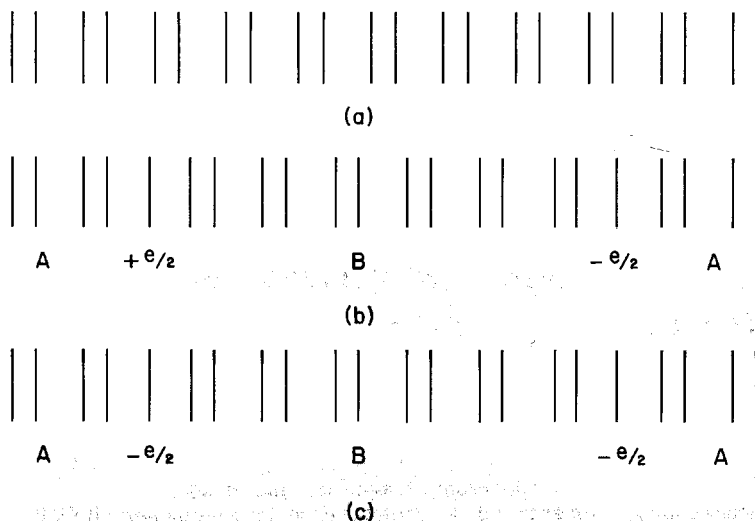
Quasi-one-dimensional metals have been extensively studied for the past decade, with examples found among organic charge transfer crystals (e.g., tetrathiofulvalene) (tetracyanoquinodimethane), (TTF)(TCNQ), organometallic complexes (e.g., $K_2Pt(CN)_4 \cdot 0.30 \cdot 2.3H_2O$, KCP) and organic polymers (e.g., polyacetylene, $(CH)_x$) /1/. For systems such as (TTF)(TCNQ) and KCP, it was found that a spontaneous symmetry breaking occurs as the temperature is decreased. That is, a periodic (Peierls) distortion of the nuclear and electron density is set up with a wavevector $q = \pm 2k_F$, where $k_F = (\pi/2)n$ is the Fermi wave vector and n is the number of carriers per unit length along the chain in the metallic state. The periodic potential generated by the distortion leads to an energy gap at the Fermi surface at $\pm k_F$.

For an incommensurate charge density wave (CDW), such as those found in (TTF)(TCNQ) and KCP, the ground state formed has no fixed phase with respect to the underlying lattice. Addition of a few excess charge carriers per unit length, c , results in shifting of k_F to $k_F = (\pi/2)(n+c)$. The plus or minus is appropriate for addition of electrons or holes. The new superlattice at $2k_F$ is at $\pi(n+c)$ and remains incommensurate with the underlying atomic potentials.

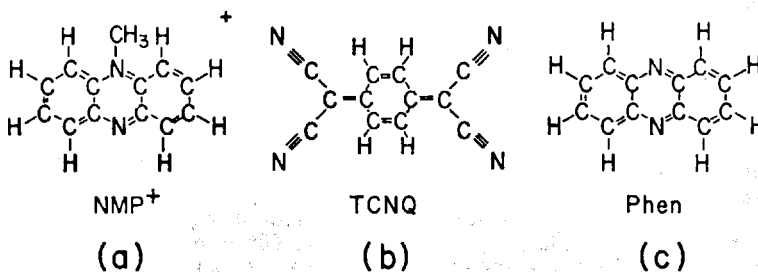
If the initial superlattice is commensurate (for example, $k_F = \pi/a$, where a is the repeat distance along the chain direction), then addition of a few extra electrons or holes will result in an incommensurate CDW (e.g., at $k_F = \pi/a(1+c)$). However, the commensurability energy strongly favors locking $2k_F$ at the zone boundary; a commensurate CDW places charge regularly at the most attractive sites in the one-dimensional lattice. For an incommensurate CDW, the maximum and minimum of charge density would not be related to atomic positions. In order to minimize the loss of commensurability energy, the "doped" chain breaks up into regions of commensurate CDW separated by charged domain walls /2/.

The success of this concept has been demonstrated for trans-polyacetylene. In this case there is a one-half filled band, and small coulomb repulsion (\bar{U}) as compared to bandwidth (W). Here the solitons are either neutral with spin 1/2 or charged $+e$ (e is the charge per electron) with no spin /3,4/. Strong support for the soliton doping mechanism comes from magnetic /5,6/, optical /7/, infrared /8/ and transport /9/ studies of this system.

Recent theoretical studies by Rice and Mele /10/ of highly correlated one-dimensional charge transfer salts near the one-quarter filled band limit have predicted the formation of solitons



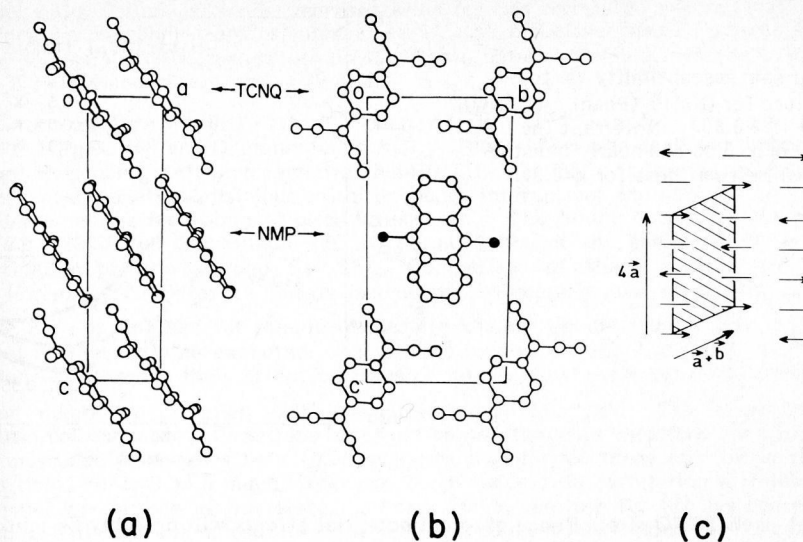
1. Schematic illustration of formation of fractionally charged solitons in highly correlated one-quarter filled band materials. (a) Uniformly dimerized commensurate Peierls ground state. (b) Formation of soliton-antisoliton pair of charge $+e/2$. Note phase of dimerization (A,B) changes as one passes through soliton. (c) Addition of electron ($-e$) to system adds to $+e/2$ site. Thus each added $-e$ charge results in two $-e/2$ solitons.



2. (a) NMP⁺; (b) TCNQ; (c) Phenazine⁰.

of fractional charge $+e/2$ in such systems as a result of doping with a small number of excess electrons or holes, photoexcitation, or thermal excitation. Figure 1 schematically illustrates the formation of a soliton-antisoliton pair in such a system. Addition of one electron ($-e$) results in two solitons of charge $-e/2$ each, as shown in Fig. 1c. Kivelson and Schrieffer have demonstrated that the $+e/2$ charge of each soliton is not just an average, but is a quantum observable of the system /11/. Similar results have been proposed for n -fold commensurate systems /12-14/.

The energy of formation of a soliton for the highly correlated one-quarter filled band is $1/2 \pi$ times the Peierls energy gap, $2 \Delta/10$. For a concentration of solitons, c , greater than the value $c^* = \Delta/\pi W$ an incommensurate lattice distortion occurs /15/. As for trans-



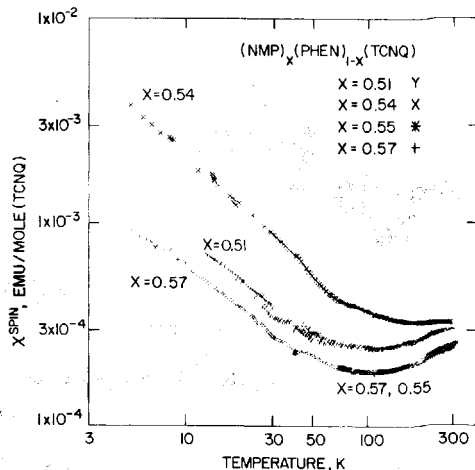
3. (a) View down the b-axis of (NMP)(TCNQ), (b) View down the highly conducting a-axis of (NMP)(TCNQ). Two methyl groups are shown for each NMP molecule, indicating their possible positions. (c) Suggested NMP and phenazine ordering in real space for $x=0.5$.

polyacetylene, the soliton is expected to delocalize over several (molecular) lattice sites.

We present here the results of an experimental study of a charge transfer salt, $(N\text{-methylphenazinium})_x (\text{Phenazine})_{1-x} (\text{TCNQ})$, $[(\text{NMP})_x (\text{Phen})_{1-x} (\text{TCNQ})]$, with $x \gtrsim 0.5$, as a function of the concentration of conduction electrons. $(\text{NMP})_{0.5} (\text{Phen})_{0.5} (\text{TCNQ})$ has been shown earlier to be a highly correlated one-quarter-filled band system. X-ray diffuse scattering and magnetic studies show that solitons are experimentally realized in this system. The range in x for formation of solitons is identified. An excess conductivity is found for those samples in which solitons have been introduced through chemical doping. Agreement of the conductivity results with a model developed by Conwell and Howard is shown.

The system studied is based upon (NMP)(TCNQ) and is achieved by substituting neutral phenazine, Phen^0 , for up to 50% of the NMP /16,17/. The Phen^0 is of similar size, shape and polarizability to NMP^+ , but unlike the NMP it contributes no carriers, Fig. 2. The overall segregated stack (NMP)(TCNQ) crystal structure /18/ (Fig. 3) remains unchanged with replacement of NMP by up to 50% Phen^0 /16,19,20/. For $x=0.5$, the NMP and phenazine alternate in a regular lattice, so that there is little disorder in this system /19,20/. Figure 3b shows the suggested NMP and Phen ordering in real space that would lead to the observed temperature independent superstructure reflections in $(\text{NMP})_{0.5} (\text{Phen})_{0.5} (\text{TCNQ})$ with respect to the (NMP)(TCNQ) Bragg spots. The four- a period of the NMP repeat along the stacking axis might suggest the presence of a commensurate potential at $4k_F$ along the TCNQ chains due to the donor chains. A sizeable value for such a potential would result in $(\text{NMP})_{0.5} (\text{Phen})_{0.5} (\text{TCNQ})$ being a semiconductor at all temperatures due to the cation potentials. However, each TCNQ stack is surrounded by four donor stacks with the TCNQ displaced by $a/2$ from the phase defined by the donor molecules. As parallel donor chains have the NMP occupation shifted by one lattice unit, the total coulomb potential at each site along a TCNQ chain due to the four neighboring chains plus farther chains will be nearly

4. Molar spin susceptibility vs. temperature for $(\text{NMP})_x(\text{Phen})_{1-x}(\text{TCNQ})$, $0.50 < x < 0.60$. Note that the data for $x=0.55$ are nearly indistinguishable from those for $x=0.57$.



identical at each TCNQ site. Hence external potential effects will probably be minimal. In addition, the charge on the NMP is significantly delocalized on the three NMP rings [21] leading to a weaker TCNQ site to TCNQ site variation of the potential due to the cations.

Upon replacement of a small number of phenazine with NMP in this limit, the full ordering of the donor stacks is retained with the few Phen's substituted by NMP's. The number of conduction electrons per unit cell to be shared among the donors and TCNQ is equal to the fraction, x , of NMP in the alloy $(\text{NMP})_x(\text{Phen})_{1-x}(\text{TCNQ})$. Generally, the values of x are accurate to ± 0.015 . Detailed x-ray diffuse scattering, optical, thermoelectric power and magnetic studies have demonstrated that the Coulomb repulsion, U , is greater than the bandwidth, $W(=4t)$, for $x \lesssim 0.67$. For $x \gtrsim 0.67$, these same experimental techniques show a crossover to a $U < W$ regime.

For $x=0.50$, temperature (T) dependent $4k_F$ x-ray diffuse scattering is observed at the commensurate $a^*/2$ value in reciprocal space (a^* is the reciprocal axis parallel to the TCNQ stacking axis) [19,20]. This T -dependent $4k_F$ scattering is further evidence that the low temperature semiconducting state in this system is the result of a Peierls distortion, not an external coulomb potential due to the donor stack. As x is increased to 0.54, the $4k_F$ scattering that is observed is broadened and remains at $a^*/2$, despite the addition of eight percent extra charges per unit cell. This broadening of the $4k_F$ scattering suggests that the disorder introduced by the additional NMP's in the donor stack leads to a reduction in the coherence length of the charge density waves occurring in the TCNQ stack. Thus x-ray diffuse scattering results show that the extra electrons go into defect states whose properties fit the predictions of solitons [10]. Further increase in x (the number of conduction electrons per unit cell) to 0.59 results in a shift of the x-ray diffuse scattering from the commensurate $0.5a^*/19,20/$.

The magnetic susceptibility, χ , was obtained as a function of temperature using a calibrated Faraday technique [6]. The core diamagnetism of phenazine and TCNQ were experimentally established (-2.20×10^{-4} emu/mole and -2.02×10^{-4} emu/mole, respectively) and, adjusting for the methyl group contribution, were subtracted from the measured total susceptibility. The results for several samples for $0.51 \lesssim x \lesssim 0.57$ are shown in Fig. 4. For x in this range, the $\chi(T)$ can be decomposed into two contributions [25] (a) a Bonner-Fisher susceptibility associated with a one-dimensional (1-D) antiferromagnetic (AFM) system, and (b) a contribution proportional to $T^{-\alpha}$, with α a constant, $0.6 \lesssim \alpha \lesssim 1$. Temperature dependent g value measurements for $x=0.51$ and $x=0.54$ verify that these spins are associated with states on the TCNQ stacks.

The data for $T > 100\text{K}$ are generally in agreement with 1DAFM behavior with an exchange interaction $J \approx 300\text{K}$, consistent with other highly correlated quarter-filled-band TCNQ salts

/25/. Assuming a Hubbard model representation for this correlated system, $J=2t^2/U$, where t is the nearest neighbor transfer integral and U the effective onsite Coulomb interaction. Using a reasonable TCNQ bandwidth of 4500K, we obtain $U \sim 8400K$. Hence $U/W > 1$ and the system is in the moderately large U/W limit.

The low temperature ($< 80K$) $\chi(T) \propto T^{-\alpha}$ behavior is well known /25/ for many TCNQ salts such as (NMP)(TCNQ) and Quinolinium(TCNQ)₂. This $\chi(T)$ can be analyzed through a random exchange Heisenberg antiferromagnetic chain (REHAF) /25/. It has been shown by earlier workers that a variety of distributions of exchange interactions can account for the data. In particular, a normalized bimodal distribution with $\sim 90\%$ of the exchange interaction being large (e.g., 230K for Quinolinium (TCNQ)₂) and $\sim 10\%$ of the exchange interaction being much smaller provide a good fit /25/. Comparison of these models to the results for (NMP)_x(Phen)_{1-x}(TCNQ) for $x \sim 0.50$ is instructive. Generally, the magnitude of the low T increase in χ is smallest for samples closest to $x=0.50$. In these cases few solitons (either chemical or thermal) are expected. As solitons involve a change in phase of dimerization, these solitons (through their effect on transfer integrals between adjacent sites) should lead to some number of smaller exchange interactions ($J=2t^2/U$). The exact form of the distribution of exchange interactions is not yet known, though it should be bimodal. The small low T increase for samples of $x \sim 0.50$ suggests that indeed there are few solitons at this composition. For $x=0.54$ a much larger low T χ is evident, in correlation with the increase in the number of solitons in this system. For $x \sim 0.55$, the low T $\chi(T)$ has decreased again, suggesting that an incommensurate CDW with few solitons has formed at this concentration. X-ray diffuse scattering for $x=0.59$ confirms /19,20/ that the system is no longer commensurate for 0.09 extra electrons per unit cell. The critical excess electron concentration for crossover from commensurate ground state with solitons to an incommensurate ground state c^* , is then ~ 0.06 /15/. This is in agreement with an estimate of $c^* = \Delta / \pi W = 0.06$ using 900K for the low temperature activation energy (see below) and 4500K for the bandwidth of TCNQ chains.

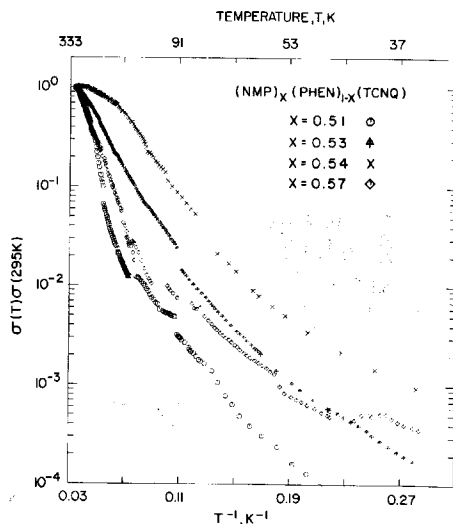
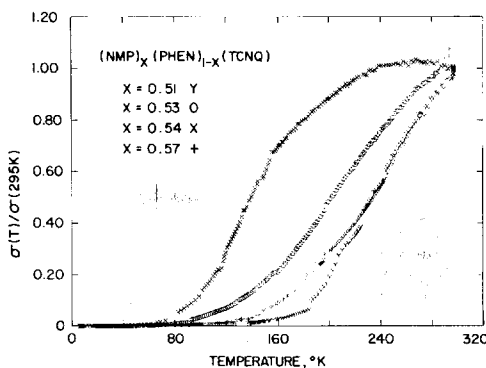
The T -dependent dc conductivity, σ , was measured using the standard four probe technique /26/. Approximately a dozen crystals of each stoichiometry were measured, with characteristic results for each x . Samples for $\sigma(T)$ were from the same synthesis used for $\chi(T)$ except for the 0.51 stoichiometry. The normalized a -axis conductivity $\sigma_n [\sigma(T) / \sigma(295K)]$ is shown in Figure 5 for $x=0.51, 0.53, 0.54$ and 0.57 . The room temperature conductivities were 4.9, 25 and 37 $\text{ohm}^{-1}\text{cm}^{-1}$ for the first three stoichiometries. Very small sample size prevented a determination of $\sigma(295K)$ for $x=0.57$. The data of Figs. 5 and 6 have been renormalized to account for jumps in $\sigma_n(T)$ associated with the formation of microcracks within these fragile crystals.

A striking aspect of $\sigma_n(T)$ is that $\sigma_n(T)$ of $x=0.57$ is strongly activated even at room temperature. The $\sigma_n(T)$ for $x=0.51$ is slightly less activated at 295K. In contrast, $\sigma(T)$ for $x=0.53$ is larger than that of $x=0.51$ and less activated, while $\sigma(T)$ for $x=0.54$ is largest in absolute value, and actually reaches a broad maximum in conductivity at 260K. Below 100K,

$\sigma(T)$ decreases for all samples. The data are replotted as $\log \sigma_n$ versus T^{-1} in Fig. 6. This clearly shows an excess conductivity for the 0.53 stoichiometry as compared to $x=0.51$ and 0.57 , and an even larger conductivity at all temperatures for $x=0.54$.

This progressive increase in the magnitude of $\sigma(T)$ as one increases from x equals 0.51 to 0.53 to 0.54 followed by the decrease for $x=0.57$ can be understood as a result of the addition of N_d electrons ($N_d = x - 0.50$) into the commensurate system and the concomitant formation of $2N_d$ $e/2$ solitons. The presence of this high density of solitons introduced by chemical doping is in addition to a T -dependent density of thermally activated (with energy $\Delta / \pi \sim 300K$) $+e/2$ and $-e/2$ soliton-antisoliton pairs. The presence of all of these states at midgap results in more electrons and fewer holes being excited. As has been shown /27-29/, evaluation of the T -dependent gap equation reveals that the critical temperature for reduction of the gap to zero is shifted to lower temperature in very good agreement with the experimental results. It is noted, that a small residual gap or pseudogap may be present at room temperature /26,30,31/

The noise power spectrum of (NMP)_x(Phen)_{1-x}(TCNQ) has been studied for $x=0.51$ and 0.53



5. Normalized a -axis conductivity vs temperature for $(\text{NMP})_x(\text{Phen})_{1-x}(\text{TCNQ})$, $0.50 < x < 0.60$.

6. Normalized a -axis conductivity vs reciprocal temperature for samples shown in Figure 5.

/32/. The results show the presence of excess f^{-1} noise in these samples, in contrast to results in commensurate systems with no chemically added solitons.

Comparison of the data for $(\text{NMP})_{0.54}(\text{Phen})_{0.46}(\text{TCNQ})$ with the corresponding results for $(\text{Quinolinium})(\text{TCNQ})_2$ shows striking similarity. This suggests that the behavior of $(\text{Quinolinium})(\text{TCNQ})_2$ and similar materials /30,31/ may also be dominated by the presence of a few chemically induced solitons that are the result of defects and/or nonstoichiometry.

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REFERENCES

- + NSF Postdoctoral Fellow, University of Florida, Gainesville, Florida. Present address, Burleigh Instruments, Fishers, N.Y. 14453 U.S.A.
1. For reviews, see Proceedings of the International Conference on Low-Dimensional Conductors, Boulder, Colorado, 1981, ed. by EPSTEIN, A.J. and CONWELL, E.M., Mol. Cryst. Liq. Cryst. 77(1981), 79, 81, 83, 85 and 86(1982); Proceedings of the NATO Advanced Study Institute on the Physics and Chemistry of Low-Dimensional Solids, Tomar, Portugal, 1981, ed. by ALCACER, L., (D. Reidel Publishing Co., Dordrecht, Holland, 1980); Highly Conducting One-Dimensional Solids, ed. by DEVREESE, J. (Plenum Press, New York, 1979), and references therein.
2. SU, W.P., KIVELSON, S. and SCHRIEFFER, J.R., Solid State Science 23(1981) 201.
3. RICE, M.J., Phys. Lett. 71A(1979) 152.
4. SU, W.P., SCHRIEFFER, J.R. and HEEGER, A.J., Phys. Rev. Lett. 42(1979) 1698.
5. IKEHATA, S., KAUFER, J., WOERNER, T., PRON, A., DRUY, M.A., SIVAK, A., HEEGER, A.J. and MACDIARMID, A.G., Phys. Rev. Lett. 45(1980) 123.
6. EPSTEIN, A.J., ROMMELMANN, H., DRUY, M.A., HEEGER, A.J. and MACDIARMID, A.G., Solid State Commun. 38(1981) 683.
7. SUZUKI, N., OZAKI, M., ETEMAD, S., HEEGER, A.J. and MACDIARMID, A.G., Phys. Rev. Lett. 45(1980) 1209.
8. HOFFMAN, D., GIBSON, H.W., EPSTEIN, A.J. and TANNER, D.B., Phys. Rev. B, in

- press; FINCHER, C.R., JR., OZAKI, M., HEEGER, A.J. and MACDIARMID, A.G., Phys. Rev. B19(1979) 4140.
9. EPSTEIN, A.J., ROMMELMANN, H., ABKOWITZ, M. and GIBSON, H.W., Phys. Rev. Lett. 47(1981) 1549; Mol. Cryst. Liq. Cryst. 77(1981) 81.
 10. RICE, M.J. and MELE, E.J., Phys. Rev. B25(1982)1339.
 11. KIVELSON, S. and SCHRIEFFER, J.R., Phys. Rev. B25(1982) 6447.
 12. SCHRIEFFER, J.R., Mol. Cryst. Liq. Cryst. 77(1981) 209.
 13. RICE, M.J., BISHOP, A.R., KRUMHANS, J.A. and TRULLINGER, S.E., Phys. Rev. Lett. 36(1976) 432.
 14. WEYL, C., JEROME, D., CHAIKIN, P.M. and BECHGAARD, K., Phys. Rev. Lett. 47(1981) 946.
 15. RICE, M.J. and MELE, E.J., Chem. Sci. 17(1981) 121. Note the value of c^* given here is one-half that given in this reference because we are dealing with spinless fermions.
 16. MILLER, J.S., and EPSTEIN, A.J., J. Am. Chem. Soc. 100(1978) 1639.
 17. EPSTEIN, A.J. and MILLER, J.S., in The Physics and Chemistry of Low-Dimensional Solids, ed. by L. Alcacer (Reidel, Boston, 1980), p. 339.
 18. POUGET, J.P., MEGTERT, S., COMES, R., and EPSTEIN, A.J., Phys. Rev. B21(1980) 486.
 19. EPSTEIN, A.J., MILLER, J.S., POUGET, J.P., and COMES, R., Phys. Rev. Lett. 47(1981) 741.
 20. POUGET, J.P., COMES, R., EPSTEIN, A.J. and MILLER, J.S., Mol. Cryst. Liq. Cryst. 85(1982) 1593.
 21. KLIMENKO, V.E. and UKRAINSKII, I.I., Zhurnal Strukturnoi Khimii 19(1978) 412.
 22. WEINSTEIN, B.A., SLADE, M.L., EPSTEIN, A.J. and MILLER, J.S., Solid State Commun. 37(1981) 643.
 23. CHAIKIN, P.M., KWAK, J.F. and EPSTEIN, A.J., Phys. Rev. Lett. 42(1979) 1178.
 24. EPSTEIN, A.J., MILLER, J.S. and CHAIKIN, P.M., Phys. Rev. Lett. 43(1979) 1178.
 25. SOOS, Z.G. and BONDESON, S.R., Mol. Cryst. Liq. Cryst. 85(1982) 1409; Phys. Rev. B22(1980) 1793; and Solid State Commun. 35(1980) 11.
 26. EPSTEIN, A.J. and MILLER, J.S., Solid State Commun. 27(1978) 325.
 27. EPSTEIN, A.J., KAUFER, J.W., ROMMELMANN, H., HOWARD, I.A., CONWELL, E.M., MILLER, J.S., POUGET, J.P. and COMES, R., Phys. Rev. Lett. 49(1982) 1037.
 28. CONWELL, E.M. and HOWARD, I.A., These proceedings.
 29. HOWARD, I.A. and CONWELL, E.M., Phys. Rev. B, in press.
 30. EPSTEIN, A.J., CONWELL, E.M. and MILLER, J.S., Ann. N.Y. Acad. Sci. 313(1978) 183.
 31. EPSTEIN, A.J. and CONWELL, E.M., Solid State Commun. 24(1977) 627.
 32. ROMMELMANN, H., KAUFER, J.W., EPSTEIN, A.J. and MILLER, J.S., These proceedings.